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A METHOD FOR ESTIMATION OF TECHNOLOGICAL AND PHYSICOCHEMICAL PROPERTIES OF CONTAINER GLASSES

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A method is developed for the calculation of characteristic temperatures, working indexes, and physicochemical properties of container glass based on the calculated effect coefficients. The estimation method can be used in production, in professional training, or in research.

Production of glass containers in Russia tends to grow, as elsewhere in the world. Factories are being upgraded, new automated lines equipped with efficient up-to-date machines and glass-melting furnaces are being installed, enterprises are restructured and renovated, and private companies invest in glass production.

The main technological requirements imposed on glass compositions and ensuring high production efficiency are as follows:

– satisfactory melting properties providing for a homogeneous and clarified glass melt;

– high working parameters making it possible to use highly efficient up-to-date glass-molding machines;

– service properties satisfying requirements imposed on glass application in various fields.

Rational selection of a composition for container glass, as a rule, requires not only a knowledge of general lines and trends in upgrading of glass compositions but also taking into account the particular production conditions.

Analysis of domestic and foreign compositions for the last 30 years [1 – 3] indicated that the prescribed technological and service parameters of glass containers can be achieved by varying the content of particular glass components within rather wide intervals (Table 1).

The compositions of glass containers produced in Western Europe show a greater stability. The prevailing compositions for container glass produced in the USA and Western Europe are lime compositions, in which alkaline-earth oxides are mainly represented by calcium oxide. In selecting the quantity of aluminum oxide, producers are usually guided by existing practice: the higher the Al_2O_3 content in a glass composition, the lower the content of SiO_2. In this way aluminum and calcium oxides form a combination: $\Sigma(SiO_2 + Al_2O_3) = 74.0 – 74.5\%$. Most producers currently prefer producing glasses containing less than 2% Al_2O_3 and $\Sigma(SiO_2 + Al_2O_3)$ equal to 74.5%.

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TABLE 1

Components	Weight content in container glass, %								
	USA			Western Europe			Eastern Europe, including Russia		
	average	minimum	maximum	average	minimum	maximum	average	minimum	maximum
SiO_2	72.15	66.20	74.70	71.91	69.02	73.93	71.66	66.76	73.40
Al_2O_3	2.07	0.87	7.13	2.00	0.92	3.83	2.08	0.69	6.14
Fe_2O_3	0.05	0.03	0.11	0.05	0.03	0.11	0.15	0.04	0.41
CaO	10.06	9.16	11.81	10.44	8.17	11.79	8.59	5.92	11.42
MgO	0.91	–	5.04	1.56	0.04	3.52	2.04	0.12	4.04
BaO	0.08	–	0.47	0.34	0.14	0.66	0.53	0.25	0.81
Na_2O	13.73	12.39	15.62	12.78	10.27	14.38	14.32	12.80	16.35
K_2O	0.57	0.12	2.93	0.77	0.19	2.08	0.55	0.09	1.67
SO_3	0.14	0.05	0.28	0.23	–	0.40	0.17	–	0.33
R_2O	14.30	12.88	17.30	13.56	11.05	15.25	14.88	12.89	16.64
RO	11.15	9.16	13.50	12.04	10.56	14.46	10.64	–	12.24
R_2O + RO	25.45	–	–	25.60	–	–	25.58	–	–

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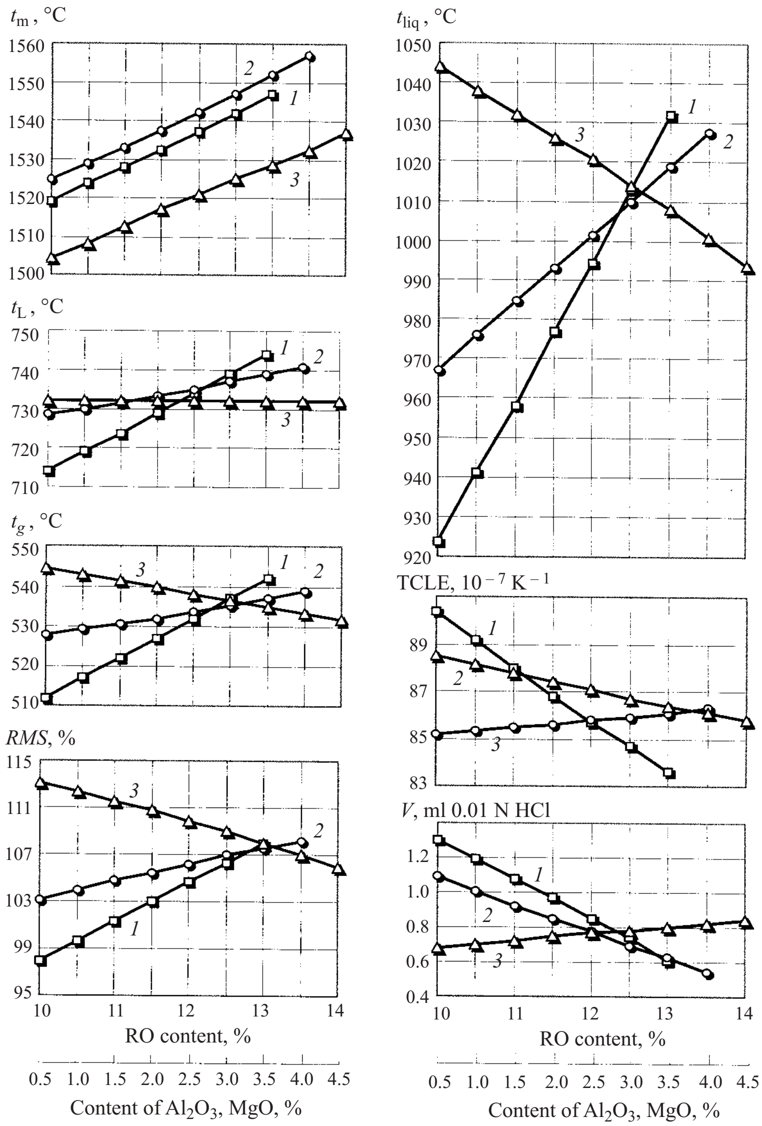

Fig. 1. Dependence of melting t_m, Littleton t_L, vitrification t_g, and liquidus t_{liq} characteristic temperatures, relative machine speed *RMS*, TCLE, and chemical resistance V on directed substitution in container glass compositions $R_2O \to RO$ (*1*), $SiO_2 \to Al_2O_3$ (*2*), and $CaO \to MgO$ (*3*).

According to the known Ditzel rule, $\Sigma(R_2O + RO)$ should be within the limits of 25.5 – 26.0% to ensure a low crystallizing capacity. Glass compositions used by virtually all manufacturers satisfy this rule.

The RO content in domestic glasses is lower than in glasses produced in the USA and Western and Eastern Europe; furthermore, container glasses in Russia typically have dolomite compositions, whereas the USA and Western Europe producers use mainly lime compositions, and Eastern European countries use lime-dolomite compositions.

It is considered expedient to use a universal glass composition for clear and tinted container glass, which would differ only in the content of pigments [3]. This makes it possible to tint the glass melt in feeders and to use glass from the same glass-melting furnace to make containers of different colors, including nontraditional tints.

The improvement of glass compositions is a topical problem for numerous producers. It is essential to know the variation regularities of physicochemical and technological properties revealed in varying oxide ratios in combinations $SiO_2 \leftrightarrow Al_2O_3$, $R_2O \leftrightarrow RO$, and $CaO \leftrightarrow MgO$. Variation limits for the content of each oxide are prescribed in accordance with Table 1 (here and elsewhere in wt.%): 69.5 – 74.0 SiO_2, 0.5 – 5.0 Al_2O_3, 6.0 – 12.0 CaO, 0.5 – 4.5 MgO, 10 – 13 Σ RO, 13.0 – 16.0 Na_2O.

The parameters of response to chemical composition variations are the estimated values of the following technological temperatures, working indexes, and physicochemical properties characterizing the efficiency of production and application of glass containers:

– technological melting temperature t_m corresponding to $\log \eta = 1$ (viscosity expressed in Pa · sec);

– drop temperature t_d, $\log \eta = 2$;

– liquidus temperature t_{liq} determining a safe interval of glass-container formation;

– Littleton temperature t_L used in calculation of working indexes, $\log \eta = 6.65$;

– vitrification temperature t_g determining the annealing regime and used in calculation of working indexes, $\log \eta = 12.3$;

– relative speed of the glass-molding machine *RMS* (%), which is the main working index determining the intensity of glass molding for a particular glass composition;

– glass density ρ (kg/m^3);

– TCLE (10^{-7} K^{-1}) characterizing the thermal resistance of a glass container;

– chemical resistance V (ml of 0.01 N HCl per 1 g of glass), which is the most significant service parameter of a glass container.

Analysis of the above parameters makes it possible to perform a quick integral evaluation of a selected glass composition; therefore, the proposed method can be regarded as universal. The determination of the specified parameters was performed using calculation methods described in [4 – 6], which have been maximally adapted to the considered range of container glass compositions.

The principle used in designing estimated matrices consisted in a directed replacement of oxides with a spacing of 0.5% within the above-mentioned combinations of oxides, while the contents of the other components remain constant (the "invariable part" of the chemical composition). At the next phase of the calculation, a similar substitution was implemented with another invariable part of the composition. For instance, in determining the effect of consecutive replacement of R_2O by RO on the selected parameters, the invariable parts of the composition had a varying ratio of SiO_2

TABLE 2

Substitution type	Effect coefficient								
	t_m, °C	t_d, °C	t_{liq}, °C	t_L, °C	t_g, °C	*RMS*, %	ρ, kg/m^3	TCLE, 10^{-7} K^{-1}	*V*, ml of 0.01 N HCl
$R_2O \to RO$	8.5	8.0	35.3	9.5	10.0	4.0	4.9	– 2.4	– 0.23
$CaO \to MgO$	7.9	7.5	– 12.4	1.2	– 2.3	– 1.7	– 4.1	– 0.7	0.04
$SiO_2 \to Al_2O_3$	9.0	6.5	17.1	3.8	2.7	1.2	3.5	0.3	– 0.16

to Al_2O_3 (while their sum remained constant) and of CaO to MgO (from dolomite to lime). The effect of variations in the combination of $SiO_2 \leftrightarrow Al_2O_3$ was also investigated with qualitatively different "invariable parts," i.e., with different ratios of R_2O to RO and CaO to MgO. Thus, compositions of container glasses with various combinations of their oxide components were analyzed. The matrices were processed using specially developed computer software.

It was found that the dependences of all parameters on deliberately performed substitutions of oxides in glass compositions are linear and differ in their direction (decreasing or increasing) and intensity. At the same time, the composition of the invariable part of glass has virtually no effect on the said parameters. Analysis of graphic dependences made it possible to determine the variation value for each property when replacing 1% of an oxide for the same quantity of another oxide, which value we call "the effect coefficient" of a particular oxide and which we recommend using in calculating the properties of container glasses (Table 2).

The principle of the proposed calculation method is not new. The methods developed by Helgof and Thomas in 1930s for the calculation of viscosity, firing temperature, and other properties of glass based on using data on a standard composition and the effect of replacement of 1% SiO_2 with other oxides [6, 7] have been used up to now.

As an example of a calculation based on the proposed method, we use a decrease in the alkaline content to 11.95% in a container glass made by the Rockware Company at the expense of introducing 1.81% MgO into the lime glass melt instead of Na_2O, which is described in the literature [1]. The variations of technological production parameters and physicochemical properties caused by the specified modification of the composition are evaluated using the proposed method.

The modification of the composition should be considered according to the following replacement scheme (%): 1.81 Na_2O replaced by 1.81 RO and then, 1.81 CaO replaced by 1.81 MgO. Table 3 shows an example of such estimation of property variations.

According to the data published by the Rockware, the drop temperature increased by 22°C, the liquidus temperature grew by 50°C, the Littleton temperature by 15°C, and the efficiency of glass-molding machines grew by 3.5% [1].

Parameters	Calculation data	Variation number
t_m, °C	1.81 × 8.5 + 1.81 × 7.9	30
t_d, °C	1.81 × 8.0 + 1.81 × 7.5	28
t_{liq}, °C	1.81 × 35.3 + 1.81 × (– 12.4)	42
t_L, °C	1.81 × 9.5 + 1.81 × 1.2	19
t_g, °C	1.81 × 10 + 1.81 × (– 2.3)	13
RMS, %	1.81 × 4 + 1.81 × (– 1.7)	4.0
ρ, kg/m^3	1.81 × 4.9 + 1.81 × (– 4.1)	1.4
TCLE, 10^{-7} °K^{-1}	1.81 × (– 2.4) + 1.81 × (– 0.7)	– 5.6
V, ml of 0.01 N HCl	1.81 × (– 0.23) + 1.81 × 0.04	– 0.34

Thus, the estimated prediction of variations of the glass properties can be regarded as quite reliable and sufficiently accurate.

The proposed calculation method can be used in production, in professional training, and also in the research and development of new compositions and upgrade of existing container-glass compositions with the aim of improving certain parameters. The calculation method is simple, accessible, fast, and does not require the use of computers.

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